Acta Crystallographica Section C
Structural Chemistry
ISSN 2053-2296

Three-dimensional hydrogen-bonded framework structures in flunarizinium nicotinate and flunarizinediium bis(4-toluenesulfonate) dihydrate

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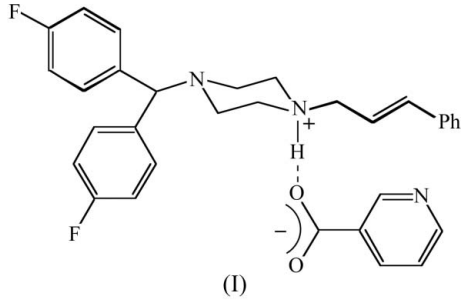
Received 15 July 2014
Accepted 16 July 2014

The structures of two salts of flunarizine, namely 1-bis[(4-fluorophenyl)methyl]-4-[(2*E*)-3-phenylprop-2-en-1-yl]piperazine, $C_{26}H_{26}F_2N_2$, are reported. In flunarizinium nicotinate {systematic name: 4-bis[(4-fluorophenyl)methyl]-1-[(2*E*)-3-phenylprop-2-en-1-yl]piperazin-1-ium pyridine-3-carboxylate}, $C_{26}H_{27}F_2N_2^+\cdot C_6H_4NO_2^-$, (I), the two ionic components are linked by a short charge-assisted N—H···O hydrogen bond. The ion pairs are linked into a three-dimensional framework structure by three independent C—H···O hydrogen bonds, augmented by C—H···π(arene) hydrogen bonds and an aromatic π–π stacking interaction. In flunarizinediium bis(4-toluenesulfonate) dihydrate {systematic name: 1-[bis(4-fluorophenyl)methyl]-4-[(2*E*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium bis(4-methylbenzenesulfonate) dihydrate}, $C_{26}H_{28}F_2N_2^{2+}\cdot 2C_7H_7O_3S^-\cdot 2H_2O$, (II), one of the anions is disordered over two sites with occupancies of 0.832 (6) and 0.168 (6). The five independent components are linked into ribbons by two independent N—H···O hydrogen bonds and four independent O—H···O hydrogen bonds, and these ribbons are linked to form a three-dimensional framework by two independent C—H···O hydrogen bonds, but C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are absent from the structure of (II). Comparisons are made with some related structures.

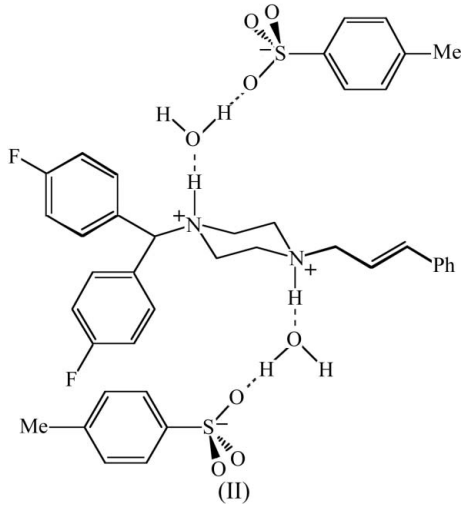
Keywords: crystal structure; flunarizinediium salt; flunarizinium salt; hydrogen bonding; π–π stacking; calcium-channel blocker.

1. Introduction

Flunarizine {systematic name: 1-[bis(4-fluorophenyl)methyl]-4-[(2*E*)-3-phenylprop-2-en-1-yl]piperazine} is a nonselective calcium-channel blocker (Amery, 1983; Fagbemi *et al.*, 1984; Tarland & Flatmark, 1999) which is effective in the prophylaxis of migraine, occlusive peripheral vascular disease and vertigo of central and peripheral origin, and also as an adjuvant in the therapy of epilepsy. Its pharmacodynamic and pharmacokinetic properties and its therapeutic use have been reviewed (Holmes *et al.*, 1984). Brief reports on the structures of several salts derived from flunarizine (Kavitha, Jasinski *et al.*, 2013; Kavitha, Yathirajan *et al.*, 2013; Shivaprakash *et al.*, 2014) and from substituted piperazine derivatives closely related to flunarizine (Kavitha, Butcher *et al.*, 2013; Kavitha, Yildirim *et al.*, 2013) have been published recently, and we report here the molecular and supramolecular structures of flunarizinium nicotinate, (I) (Fig. 1), and flunarizinediium bis(4-toluenesulfonate) dihydrate, (II) (Fig. 2). The main purposes of the present study are, firstly, to compare the supramolecular assemblies of (I) and (II), and, secondly, to compare the structures of (I) and (II) with those of some closely related analogues.



(I)



(II)

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of salt (I), flunarizine free base (4.05 g, 0.01 mol) and nicotinic acid (1.23 g, 0.01 mol) were dissolved in hot dimethylformamide (5 ml) and the solution was stirred for 10 min. The solution was then allowed to cool slowly to ambient temperature in the presence of air. Colourless crystals of (I) suitable for single-crystal X-ray diffraction appeared after a few days and were collected by filtration (m.p. 383–

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{26}H_{27}F_2N_2^+\cdot C_6H_4NO_2^-$	$C_{26}H_{28}F_2N_2^{2+}\cdot 2C_7H_7O_3S^-\cdot 2H_2O$
M_r	527.60	784.91
Crystal system, space group	Monoclinic, *Pc*	Monoclinic, $P2_1/c$
Temperature (K)	200	200
a, *b*, *c* (Å)	10.8536 (4), 10.8103 (4), 11.3901 (4)	10.0546 (5), 14.8338 (6), 26.9437 (12)
β (°)	92.717 (2)	106.497 (3)
V (Å^3)	1334.91 (8)	3853.2 (3)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.20
Crystal size (mm)	0.54 × 0.49 × 0.13	0.59 × 0.43 × 0.24
Data collection		
Diffractometer	Bruker APEXII CCD area-detector diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.873, 0.988	0.877, 0.953
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	23278, 6092, 5770	45646, 7212, 6219
R_{int}	0.027	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.668	0.607
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.081, 1.03	0.075, 0.202, 1.09
No. of reflections	6092	7212
No. of parameters	352	527
No. of restraints	2	27
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.18	0.71, −0.60
Absolute structure	Flack *x* parameter (Flack, 1983) determined using 2539 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	0.10 (15)	–

Computer programs: *APEX2* (Bruker, 2010), *SAINT* (Bruker, 2010), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

385 K). For the synthesis of hydrated salt (II), flunarizine free base (4.05 g, 0.01 mol) and 4-toluenesufonic acid monohydrate (1.72 g, 0.009 mol) were dissolved in hot methanol (20 ml) and the solution was stirred for 10 min. The solution was then allowed to cool slowly to ambient temperature in the presence of air. Yellow crystals of (II) suitable for single-crystal X-ray diffraction appeared after a few days and were collected by filtration (m.p. 406–410 K).

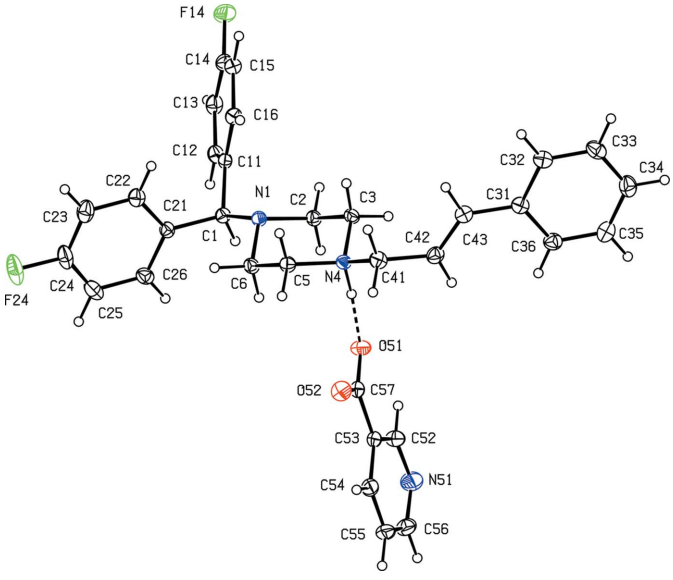


Figure 1
The independent components of salt (I), showing the atom-labelling scheme and the N—H···O hydrogen bond (dashed line) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms. C-bound H atoms were treated as riding in geometrically idealized positions, with C—H = 0.95 (alkenyl and aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic CH), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other C-bound H atoms. N- and O-bound H atoms were permitted to ride at the positions located in difference maps, with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O), giving the N—H and O—H distances shown in Tables 2 and 3. For (I), the correct orientation of the structure with respect to the polar-axis direction was established by means of the Flack *x* parameter (Flack, 1983), determined as *x* = 0.09 (15) by the use of 2539 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013) from a total of 2758 Bijvoet pairs (83% coverage), and by the use of the Hooft *y* parameter (Hooft *et al.*, 2008), calculated as 0.10 (17), also using 2758 Bijvoet pairs. For hydrated salt (II), the crys-

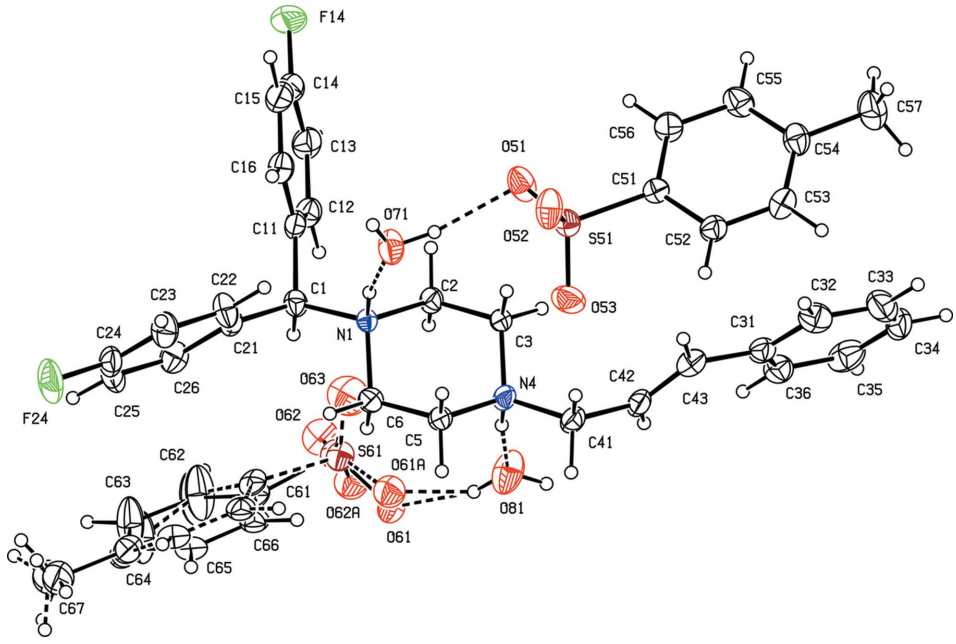


Figure 2
The independent components of hydrated salt (II), showing the atom-labelling scheme and the O—H···O and N—H···O hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and the site occupancies for the two orientations of the disordered anion are 0.832 (6) and 0.168 (6). The pairs of atomic sites S61 and S61*A*, and O63 and O63*A*, are nearly coincident and, for the sake of clarity, the atom labels C61*A*–C67*A*, S61*A* and O63*A* have been omitted.

tals were all of very indifferent quality and about a dozen individual crystals were subjected to preliminary examination using polarizing microscopy; none showed any visible signs of twinning or intergrowth. Three data sets were obtained from the two most promising looking crystals and the refinement reported here results from the best of these data sets, although all three gave essentially identical solutions. For all three data sets, it was apparent from an early stage that one of the anions, that containing atom S61 (Fig. 2), was disordered over two sets of sites. For the minor orientation, the directly bonded distances and the one-angle distances were restrained to be equal to the corresponding distances in the major orientation, subject to standard uncertainties of 0.005 and 0.01 Å, respectively. In addition, the anisotropic displacement parameters for the corresponding pairs of partial-occupancy atoms which occupied approximately the same regions of physical space were constrained to be identical. Subject to these conditions, the site occupancies for the two orientations refined to 0.832 (6) and 0.168 (6). Because of the rather weak diffraction at high angles, all reflections having $\theta > 25.5°$ were omitted from the final refinements for hydrated salt (II). Examination of the refined structures of (I) and (II) using *PLATON* (Spek, 2009) showed an absence of any solvent-accessible voids for both structures. For the rerefinement of (VI) (see *Results and discussion*, §3), the reported unit cell in the space group $P2_1/n$ (Kavitha, Butcher *et al.*, 2013) was transformed to the $P2_1/c$ setting with dimensions a = 10.0845 (2) Å, b = 14.6026 (3) Å, c = 27.1907 (7) Å and β = 108.315 (2)°.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

*Cg*1 and *Cg*2 represent the centroids of the C11–C16 and C31–C36 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O51	0.98	1.58	2.5630 (19)	175
C3—H3*B*···O52^{i}	0.99	2.53	3.440 (2)	153
C13—H13···O52^{ii}	0.95	2.57	3.442 (2)	152
C56—H56···O51^{iii}	0.95	2.34	3.236 (3)	158
C26—H26···*Cg*1^{iv}	0.95	2.81	3.758 (2)	173
C55—H55···*Cg*2^{v}	0.95	2.85	3.567 (2)	133

Symmetry codes: (i) $x, -y+1, z+\frac{1}{2}$; (ii) $x-1, -y+1, z+\frac{1}{2}$; (iii) $x, -y+2, z-\frac{1}{2}$; (iv) $x, -y+1, z-\frac{1}{2}$; (v) $x, y, z-1$.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O71	0.93	1.79	2.716 (4)	169
N4—H4···O81	1.00	1.69	2.690 (4)	173
O71—H71*A*···O51	0.85	1.88	2.708 (4)	167
O71—H71*B*···O61^{i}	0.84	1.87	2.675 (5)	160
O81—H81*A*···O61	0.84	2.05	2.852 (5)	161
O81—H81*B*···O52^{ii}	0.84	1.92	2.748 (4)	167
C1—H1*A*···O63	1.00	2.23	3.139 (7)	151
C2—H2*B*···O63	0.99	2.47	3.314 (7)	143
C6—H6*A*···O53^{iii}	0.99	2.37	3.191 (5)	140
C16—H16···O62^{i}	0.95	2.41	3.228 (6)	144
C22—H22···O71	0.95	2.49	3.381 (5)	156
C34—H34···O51^{iv}	0.95	2.42	3.362 (6)	169
C41—H41*A*···O53	0.99	2.35	3.280 (5)	157
C41—H41*B*···O61^{v}	0.99	2.37	3.341 (5)	167

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $-x+2, -y+1, -z$; (iv) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+1, -y+1, -z$.

3. Results and discussion

Salt (I) consists of flunarizinium monocations, in which protonation of the flunarizine free base has occurred selectively at atom N4, which is the N atom more remote from the electronegative fluorophenyl units, and nicotinate anions; the asymmetric unit was selected such that the two ions within it are linked by an N—H···O hydrogen bond (Fig. 1 and Table 2). The constitution of (II) is more complex, comprising a flunarizinediium dication, two 4-methylbenzenesulfonate anions, one of which exhibits positional disorder, and two water molecules. Accordingly, there is considerable flexibility in the choice of the asymmetric unit. However, it is possible to specify a reasonably compact asymmetric unit within which the five independent components are linked by N—H···O and O—H···O hydrogen bonds (Fig. 2 and Table 3).

In each of (I) and (II), the pyrazine ring adopts a chair conformation, with the two hydrocarbyl substituents occupying equatorial sites (Figs. 1 and 2). The ring-puckering parameters (Cremer & Pople, 1975), calculated for the atom sequence N1–C2–C3–N4–C5–C6, are Q = 0.5934 (17) Å, θ = 3.56 (15)° and φ = 345 (3)° for (I), and Q = 0.554 (3) Å, θ = 3.0 (3)° and φ = 326 (8)° for (II). For an ideal chair conformation, the value of θ is exactly zero (Boeyens, 1978).

The 3-phenylprop-2-en-1-yl substituents in (I) and (II) adopt very similar orientations relative to the piperazine ring and very similar overall conformations, as shown by the relevant torsion angles (Tables 4 and 5). On the other hand, the orientations of the two independent fluorophenyl rings are somewhat different in the two compounds. This may be ascribed, at least in part, to the different direction-specific interactions involving these rings in the two compounds, including the C—H···O and C—H···π(arene) hydrogen bonds and the aromatic π–π stacking interactions, which differ markedly between the two compounds, as discussed below. There is no internal symmetry in the cation in either compound, so that these cations are conformationally chiral. However, in each case, the presence of glide planes confirms that equal numbers of the two conformational enantiomers are present.

Within the selected asymmetric unit of (I) (Fig. 1), the two components are linked by a rather short and nearly linear charge-assisted (Gilli *et al.*, 1994) N—H···O hydrogen bond

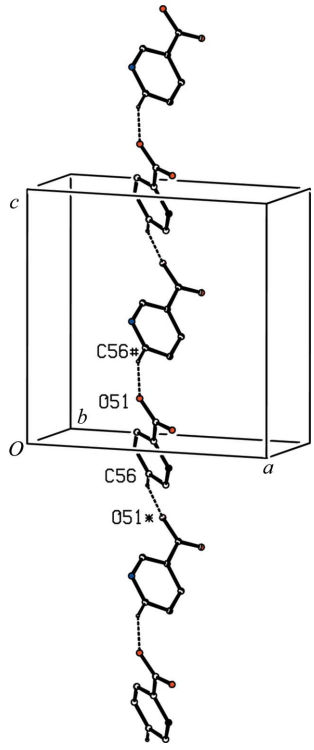


Figure 3
Part of the crystal structure of salt (I), showing the formation of a hydrogen-bonded $C(7)$ chain parallel to [001] and built from nicotinate anions only. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk or a hash symbol (#) are at the symmetry positions (x, $-y+2$, $z-\frac{1}{2}$) and (x, $-y+2$, $z+\frac{1}{2}$), respectively.

(Table 2). Ion pairs of this type are linked by three independent C—H···O hydrogen bonds (Table 2) to form a three-dimensional framework structure, the formation of which is

Table 4
Selected torsion angles (°) for (I).

C2—N1—C1—C11	−70.92 (16)	C3—N4—C41—C42	−55.58 (19)
C2—N1—C1—C21	165.22 (13)	N4—C41—C42—C43	118.27 (19)
N1—C1—C11—C12	150.17 (15)	C41—C42—C43—C31	177.23 (16)
N1—C1—C21—C22	69.4 (2)	C42—C43—C31—C32	−178.93 (18)

Table 5
Selected torsion angles (°) for (II).

C2—N1—C1—C11	−51.9 (4)	C3—N4—C41—C42	−56.2 (4)
C2—N1—C1—C21	−179.0 (3)	N4—C41—C42—C43	121.6 (4)
N1—C1—C11—C12	101.8 (4)	C41—C42—C43—C31	172.9 (3)
N1—C1—C21—C22	42.4 (5)	C42—C43—C31—C32	−167.1 (4)

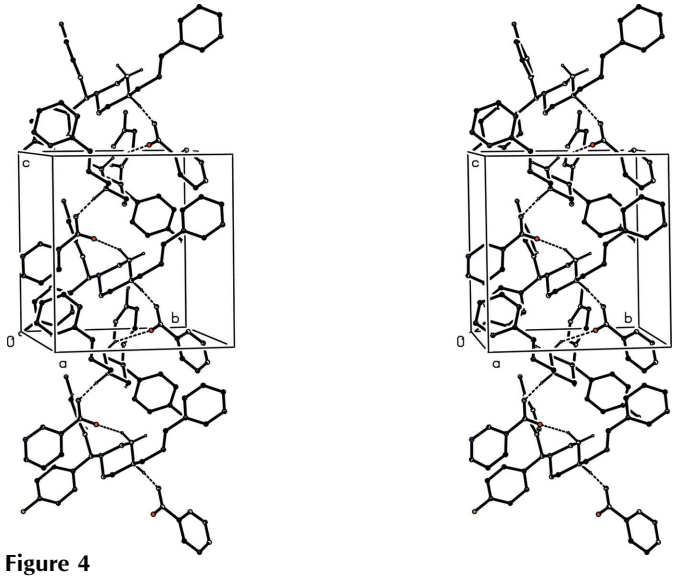


Figure 4
A stereoview of part of the crystal structure of salt (I), showing the formation of a hydrogen-bonded $C_2^2(7)$ chain parallel to [001] and containing alternating C—H···O and N—H···O hydrogen bonds, shown as dashed lines. For the sake of clarity, H atoms bonded to C atoms which are not involved in the motif shown have been omitted.

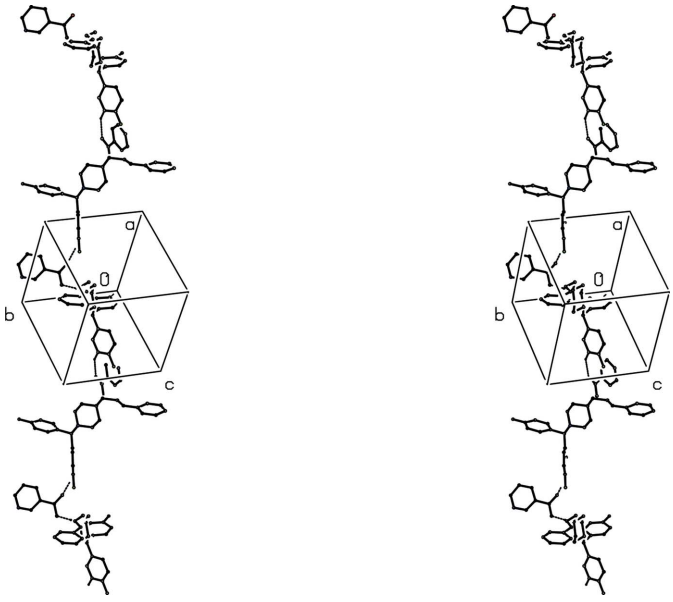


Figure 5
A stereoview of part of the crystal structure of salt (I), showing the formation of a hydrogen-bonded $C_2^2(13)$ chain parallel to $[20\overline{1}]$ and containing alternating C—H···O and N—H···O hydrogen bonds, shown as dashed lines. For the sake of clarity, H atoms bonded to C atoms which are not involved in the motif shown have been omitted.

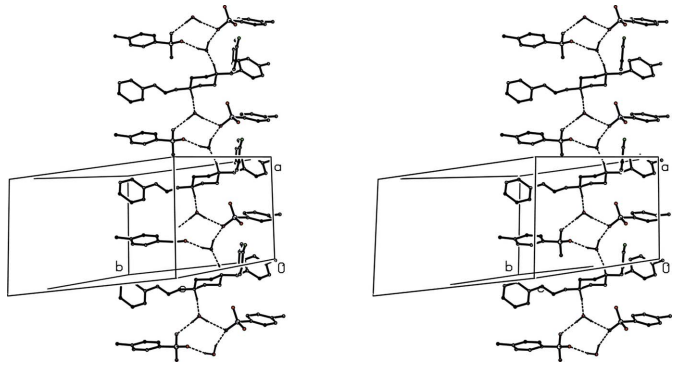


Figure 6
A stereoview of part of the crystal structure of hydrated salt (II), showing the formation of a hydrogen-bonded ribbon parallel to [100]. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted and only the major orientation of the disordered anion is shown.

readily analysed in terms of three fairly simple one-dimensional substructures (Ferguson *et al.*, 1998*a*,*b*; Gregson *et al.*, 2000). The simplest of these substructures involves only the nicotinate component, where anions related by the *c*-glide plane at $y = 1$ are linked into a $C(7)$ chain (Bernstein *et al.*, 1995) running parallel to the [001] direction (Fig. 3). The C—H···O hydrogen bond having atom C3 as the donor, together with the N—H···O hydrogen bond, link ion pairs related by the *c*-glide plane at $y = \frac{1}{2}$ to form a $C_2^2(7)$ chain, also running parallel to the [001] direction (Fig. 4). The combination of the two chain motifs parallel to [001] generates a sheet lying parallel to (100) and such sheets are linked by the third one-dimensional substructure. In this final substructure, the C—H···O hydrogen bond having atom C13 as the donor links ion pairs, again related by the *c*-glide plane at $y = \frac{1}{2}$, but this time forming a $C_2^2(13)$ chain running parallel to the $[20\overline{1}]$ direction (Fig. 5), so completing the formation of the three-dimensional structure.

The resulting framework of (I) is modestly reinforced by two fairly long C—H···π(arene) hydrogen bonds (Table 2) and by an aromatic π–π stacking interaction. Between the C21–C26 ring in the cation at (x, y, z) and the C31–C36 ring in the cation at $(-1 + x, 1 - y, -\frac{1}{2} + z)$ there is a ring-centroid separation of 3.6986 (11) Å. The dihedral angle between the ring planes is 5.02 (9)° and the shortest perpendicular distance from the centroid of one ring to the plane of the other is 3.3875 (8) Å, corresponding to a nearly ideal ring-centroid offset of *ca* 1.48 Å.

In (II), the five independent components are again linked into a three-dimensional framework structure by a combination of O—H···O, N—H···O and C—H···O hydrogen bonds (Table 3), although C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are absent from the structure. The framework of (II) is considerably more complex than that of (I) but, as for (I), its formation can readily be analysed in terms of low-dimensional substructures. The principal substructure involves only O—H···O and N—H···O hydrogen bonds. The five-component aggregates (Fig. 2), which are related by translation along [100], are linked to form a broad ribbon in which the cations, acting as twofold donors in N—H···O hydrogen bonds, alternate with $R_4^3(10)$ rings built from the two independent anions and the two independent water molecules (Fig. 6). Four of these ribbons pass through each unit cell, with the hydrogen bonds lying approximately along the lines $(x, 0.4, 0.1)$, $(x, 0.9, 0.4)$, $(x, 0.6, 0.9)$ and $(x, 0.1, 0.6)$.

The structure of (II) contains a number of short intermolecular C—H···O contacts (Table 3). However, the majority of these lie either within the selected asymmetric unit or within the ribbon built from the O—H···O and N—H···O hydrogen bonds, or they have C—H···O angles close to 140°, such that they cannot be regarded as structurally significant (Wood *et al.*, 2009). Hence, the only two of these interactions which can be regarded as structurally significant hydrogen bonds influencing the overall dimensionality of the supramolecular assembly are those having atoms O51 and O61 as the acceptors, and each of these hydrogen bonds can be regarded as the basis of a simple substructure.

The C—H···O hydrogen bond involving atom O51 leads to the formation of a $C_3^2(16)$ chain running parallel to the [010] direction, comprising only the cation, the anion containing atom S51 and the water molecule containing atom O71, and built from components related by the 2_1 screw axis along $(0, y, \frac{1}{4})$ (Fig. 7). The effect of this chain motif is to link the [100] chains in the domain $0 < z < \frac{1}{2}$ into a sheet lying parallel to (001). A second sheet of this type, related to the first by inversion, lies in the domain $\frac{1}{2} < z < 1.0$. The final substructure involves, in addition to the cation, the anion containing atom S61 and the water molecule containing atom O81 (*i.e.* those

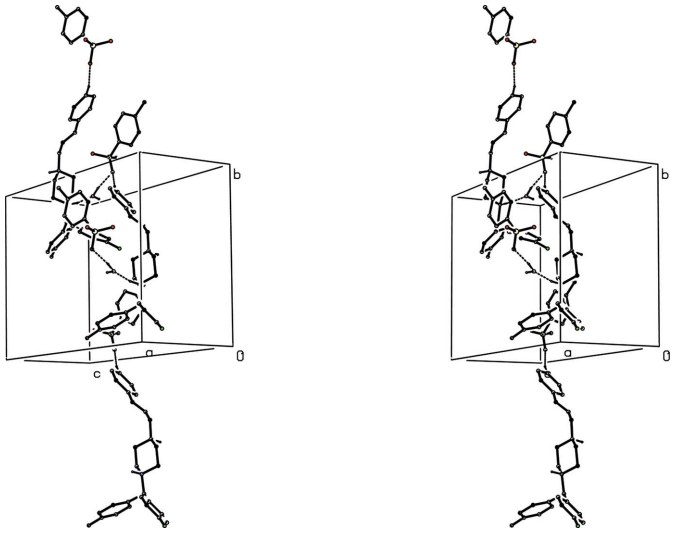


Figure 7
A stereoview of part of the crystal structure of hydrated salt (II), showing the formation of a hydrogen-bonded $C_3^2(16)$ chain parallel to [010] and incorporating the cation and only one type each of the independent anions and water molecule. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

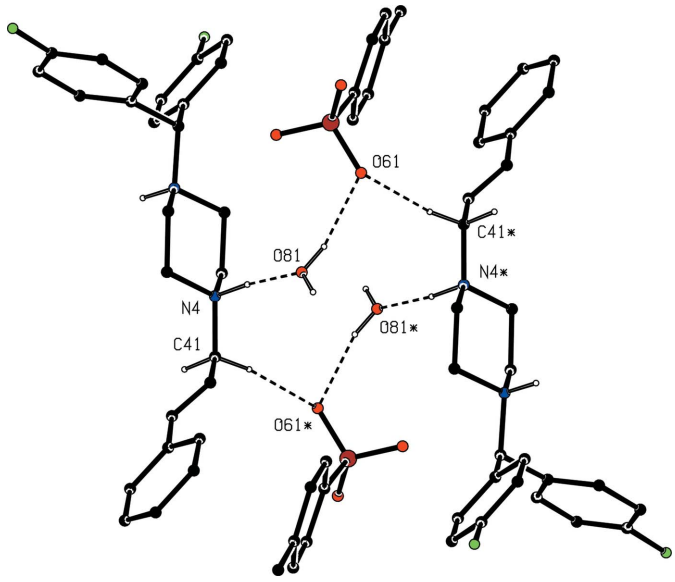


Figure 8
Part of the crystal structure of hydrated salt (II), showing the formation of a centrosymmetric hydrogen-bonded $R_6^4(14)$ motif which links adjacent (001) sheets. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, components not involved in the motif shown and H atoms bonded to C atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk are at the symmetry position $(-x + 1, -y + 1, -z)$.

not participating in the chain along [010]), and it takes the form of a finite zero-dimensional motif characterized by an $R_6^4(14)$ ring (Fig. 8). The effect of this ring motif is to link directly the sheet in the domain $0 < z < \frac{1}{2}$ with two adjacent sheets in the domains $\frac{1}{2} < z < 1.0$ and $-\frac{1}{2} < z < 0$, so completing the formation of the three-dimensional framework structure.

It is of interest briefly to compare the supramolecular assembly in some closely-related compounds with that reported here for (I) and (II). Flunarizine forms 1:1 salts with both succinic and maleic acids, and in flunarizinium hydrogen succinate, (III) (Kavitha, Yathirajan *et al.*, 2013), the anion adopts an extended chain conformation such that the carboxylic acid –OH group is available as a donor in the formation of inter-anion O—H···O hydrogen bonds. By contrast, the anion in flunarizinium hydrogen maleate, (IV) (Kavitha, Jasinski *et al.*, 2013), contains a short intra-anion O—H···O hydrogen bond, forming an $S(7)$ motif, and the carboxylic acid –OH group is not available as a donor for the formation of hydrogen bonds with other entities in the structure. In (III), a combination of O—H···O, N—H···O and C—H···O hydrogen bonds links the component ions into a three-dimensional framework structure. The supramolecular structure of (IV) was described in the original report as a chain, but re-examination of this structure using the published atomic coordinates shows the structure to consist of a ribbon built from alternating edge-fused $S(7)$ and $R_3^3(11)$ rings (Fig. 9). In flunarizinediium dichloride hemihydrate, (V) (Shivaprakash *et al.*, 2014), the independent ionic components are linked by two nearly-linear charge-assisted N—H···Cl hydrogen bonds and symmetry-related pairs of these ion triplets are linked by O—H···Cl hydrogen bonds, where the donor is a water molecule lying across a twofold rotation axis, to form a seven-component aggregate. Two independent and nearly linear C—H···Cl hydrogen bonds link these aggregates into a complex ribbon. There are also two short C—H···O contacts in the structure of (V), but in each the H···O distance (2.67 and 2.68 Å) exceeds the sum of the van der Waals radii (2.61 Å; Bondi, 1964; Rowland & Taylor, 1996) while having C—H···O angles close to 140° (*cf.* Wood *et al.*, 2009), so that neither of these contacts is structurally significant.

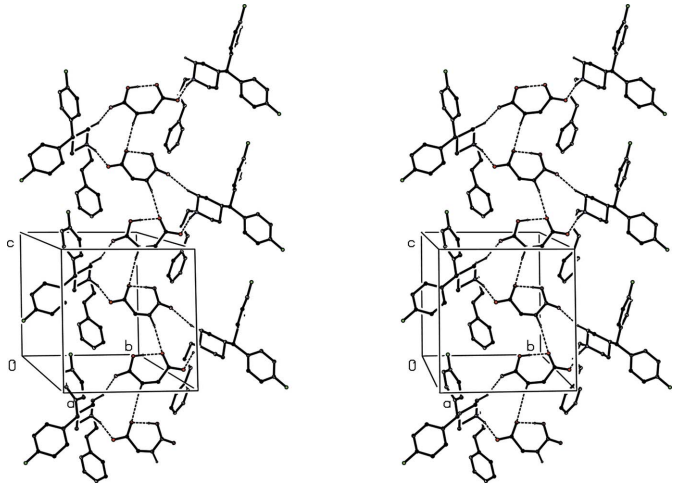


Figure 9
A stereoview of part of the crystal structure of (IV), showing the formation of a hydrogen-bonded ribbon containing alternating $S(7)$ and $R_3^3(11)$ rings. The original atomic coordinates (Kavitha, Jasinski *et al.*, 2013) have been used. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Cinnarizine {systematic name: 1-diphenylmethyl-4-[(2*E*)-3-phenylprop-2-en-1-yl]piperazine} is also a calcium-channel blocker, which differs from flunarizine only in the absence of the 4-fluoro substituents in the diarylmethyl unit. Cinnarizine forms a dihydrated 1:2 salt, (VI), with 4-toluenesulfonic acid (Kavitha, Butcher *et al.*, 2013). Compound (VI) appears to be isomorphous with (II), although it was refined in the alternative $P2_1/n$ setting, rather than in $P2_1/c$ as for (II). There is very little discussion of the supramolecular assembly in the original report, apart from a listing of the O—H···O and N—H···O hydrogen bonds, while C—H···O hydrogen bonds were not mentioned. Re-examination of the supramolecular assembly of (VI) using the published atomic coordinates shows that it contains the same type of ribbon along [100], built from O—H···O and N—H···O hydrogen bonds, as found here for (II) (*cf.* Fig. 6). In addition, there are two significant C—H···O hydrogen bonds in the structure of (VI), one of which generates a $C_3^2(16)$ chain running parallel to [010], while the other generates a centrosymmetric $R_6^4(14)$ motif, entirely comparable with the action of the corresponding hydrogen bonds in (II) (*cf.* Figs. 7 and 8). Hence (II) and (VI) are isostructural, as confirmed by a new refinement for (VI) carried out in the space group $P2_1/c$ using the deposited structure-factor data. This refinement, using the coordinates of (II) as the starting point, but with the two F atoms replaced by H atoms, converged to $R = 0.0197$ for 7891 observed reflections and 509 parameters subject to 27 restraints, with refined site occupancies for the disordered anion of 0.804 (2) and 0.196 (2), thus demonstrating clearly the isostructural nature of (II) and (VI). It is noteworthy that the absence of F substituents from (VI) appears to have no significant influence on the structure, apart from the minor and expected difference in the unit-cell volumes for (II) and (VI), *viz.* 3853.2 (3) Å^3 at 200 (2) K and 3801.25 (14) Å^3 at 100 (2) K, respectively.

CNK thanks the University of Mysore for research facilities and is grateful to the Principal, Maharani's Science College for Women, Mysore, for giving permission to carry out this research.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SK3553).

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supporting information

Acta Cryst. (2014). C**70**, 805-811 [doi:10.1107/S2053229614016532]

Three-dimensional hydrogen-bonded framework structures in flunarizinium nicotinate and flunarizinediium bis(4-toluenesulfonate) dihydrate

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2014); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

(I) 4-Bis[(4-fluorophenyl)methyl]-1-[(2*E*)-3-phenylprop-2-en-1-yl]piperazin-1-ium pyridine-3-carboxylate

Crystal data

$C_{26}H_{27}F_2N_2\cdot C_6H_4NO_2$
M_r = 527.60
Monoclinic, *Pc*
a = 10.8536 (4) Å
b = 10.8103 (4) Å
c = 11.3901 (4) Å
β = 92.717 (2)°
V = 1334.91 (8) Å^3
Z = 2
F(000) = 556
D_x = 1.313 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 6092 reflections
θ = 1.9–28.4°
μ = 0.09 mm^{-1}
T = 200 K
Plate, colourless
0.54 × 0.49 × 0.13 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.873, T_{max} = 0.988
23278 measured reflections
6092 independent reflections
5770 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 28.4°, θ_{min} = 1.9°
h = −14→14
k = −14→14
l = −15→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.081
S = 1.03
6092 reflections
352 parameters
2 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.1632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Absolute structure: Flack *x* parameter (Flack, 1983) determined using 2539 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.10 (15)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.17850 (12)	0.43015 (13)	0.31935 (12)	0.0250 (3)
C2	0.19249 (15)	0.55279 (15)	0.37393 (15)	0.0261 (3)
H2A	0.1416	0.5572	0.4437	0.031*
H2B	0.1625	0.6169	0.3175	0.031*
C3	0.32579 (15)	0.57830 (16)	0.41056 (14)	0.0268 (3)
H3A	0.3330	0.6617	0.4462	0.032*
H3B	0.3547	0.5170	0.4703	0.032*
N4	0.40422 (12)	0.57106 (13)	0.30680 (12)	0.0244 (3)
H4	0.3770	0.6362	0.2515	0.029*
C5	0.38561 (15)	0.44918 (16)	0.24771 (15)	0.0276 (3)
H5A	0.4157	0.3824	0.3012	0.033*
H5B	0.4341	0.4463	0.1763	0.033*
C6	0.25047 (15)	0.42811 (16)	0.21400 (15)	0.0273 (3)
H6A	0.2206	0.4936	0.1589	0.033*
H6B	0.2400	0.3472	0.1740	0.033*
C1	0.04617 (14)	0.40285 (15)	0.29532 (15)	0.0250 (3)
H1	0.0071	0.4774	0.2573	0.030*
C11	−0.01644 (14)	0.37958 (15)	0.41020 (15)	0.0251 (3)
C12	−0.14102 (15)	0.40862 (16)	0.41860 (16)	0.0302 (4)
H12	−0.1844	0.4472	0.3541	0.036*
C13	−0.20273 (17)	0.38200 (18)	0.51973 (18)	0.0358 (4)
H13	−0.2879	0.4003	0.5247	0.043*
C14	−0.13720 (18)	0.32879 (16)	0.61156 (17)	0.0345 (4)
F14	−0.19601 (13)	0.30702 (13)	0.71334 (11)	0.0516 (3)
C15	−0.01478 (18)	0.29758 (17)	0.60796 (17)	0.0336 (4)
H15	0.0275	0.2594	0.6733	0.040*
C16	0.04540 (16)	0.32364 (16)	0.50559 (16)	0.0294 (3)
H16	0.1301	0.3028	0.5009	0.035*
C21	0.02675 (15)	0.29468 (16)	0.21188 (14)	0.0265 (3)
C22	0.05734 (17)	0.17386 (17)	0.24553 (18)	0.0346 (4)
H22	0.0922	0.1585	0.3222	0.041*
C23	0.0372 (2)	0.07615 (19)	0.1681 (2)	0.0435 (5)
H23	0.0577	−0.0061	0.1911	0.052*
C24	−0.01274 (19)	0.1004 (2)	0.0577 (2)	0.0454 (5)
F24	−0.03385 (15)	0.00390 (16)	−0.01654 (15)	0.0702 (5)

C25	−0.04382 (18)	0.2171 (2)	0.02057 (18)	0.0437 (5)
H25	−0.0782	0.2311	−0.0565	0.052*
C26	−0.02378 (17)	0.31482 (19)	0.09868 (16)	0.0334 (4)
H26	−0.0449	0.3965	0.0745	0.040*
C41	0.53859 (16)	0.58793 (18)	0.34023 (17)	0.0321 (4)
H41A	0.5671	0.5174	0.3899	0.039*
H41B	0.5860	0.5870	0.2681	0.039*
C42	0.56485 (16)	0.70599 (18)	0.40543 (17)	0.0327 (4)
H42	0.5461	0.7823	0.3673	0.039*
C43	0.61323 (16)	0.70778 (17)	0.51436 (16)	0.0313 (4)
H43	0.6269	0.6293	0.5502	0.038*
C31	0.64836 (15)	0.81561 (17)	0.58665 (15)	0.0299 (4)
C32	0.70012 (17)	0.79671 (19)	0.69949 (17)	0.0342 (4)
H32	0.7088	0.7147	0.7287	0.041*
C33	0.73911 (18)	0.8947 (2)	0.77006 (18)	0.0401 (4)
H33	0.7747	0.8797	0.8466	0.048*
C34	0.72614 (19)	1.0147 (2)	0.7288 (2)	0.0425 (4)
H34	0.7532	1.0824	0.7767	0.051*
C35	0.67351 (19)	1.03563 (19)	0.6173 (2)	0.0417 (4)
H35	0.6637	1.1180	0.5893	0.050*
C36	0.63521 (18)	0.93764 (18)	0.54642 (18)	0.0354 (4)
H36	0.5998	0.9532	0.4700	0.042*
N51	0.26141 (19)	1.03197 (17)	−0.06212 (17)	0.0492 (5)
C52	0.28936 (19)	0.93447 (18)	0.00654 (17)	0.0370 (4)
H52	0.2473	0.9261	0.0774	0.044*
C53	0.37557 (16)	0.84493 (16)	−0.01882 (15)	0.0290 (3)
C54	0.43615 (18)	0.85725 (19)	−0.12234 (17)	0.0378 (4)
H54	0.4972	0.7991	−0.1426	0.045*
C55	0.4063 (2)	0.9557 (2)	−0.19576 (19)	0.0464 (5)
H55	0.4447	0.9650	−0.2685	0.056*
C56	0.3202 (2)	1.0397 (2)	−0.1618 (2)	0.0480 (5)
H56	0.3015	1.1076	−0.2125	0.058*
C57	0.40362 (16)	0.73877 (16)	0.06383 (15)	0.0278 (3)
O51	0.33722 (13)	0.73420 (12)	0.15347 (11)	0.0360 (3)
O52	0.48540 (13)	0.66376 (13)	0.04174 (13)	0.0407 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0236 (6)	0.0273 (7)	0.0243 (7)	−0.0025 (5)	0.0046 (5)	−0.0024 (5)
C2	0.0252 (7)	0.0279 (8)	0.0255 (8)	−0.0009 (6)	0.0040 (6)	−0.0033 (6)
C3	0.0277 (8)	0.0318 (8)	0.0212 (8)	−0.0038 (6)	0.0037 (6)	−0.0027 (6)
N4	0.0222 (6)	0.0288 (7)	0.0222 (7)	−0.0022 (5)	0.0019 (5)	0.0008 (5)
C5	0.0259 (8)	0.0296 (8)	0.0277 (8)	−0.0003 (6)	0.0053 (6)	−0.0025 (7)
C6	0.0262 (8)	0.0316 (8)	0.0245 (8)	−0.0026 (6)	0.0046 (6)	−0.0039 (6)
C1	0.0230 (7)	0.0257 (7)	0.0262 (8)	−0.0001 (6)	0.0008 (6)	0.0006 (6)
C11	0.0247 (7)	0.0235 (7)	0.0274 (8)	−0.0033 (6)	0.0028 (6)	−0.0037 (6)
C12	0.0245 (7)	0.0332 (8)	0.0327 (9)	−0.0001 (6)	0.0000 (6)	−0.0040 (7)

C13	0.0271 (8)	0.0378 (9)	0.0432 (10)	−0.0044 (7)	0.0089 (7)	−0.0084 (8)
C14	0.0405 (9)	0.0319 (8)	0.0323 (9)	−0.0098 (7)	0.0141 (7)	−0.0047 (7)
F14	0.0582 (8)	0.0568 (8)	0.0419 (7)	−0.0109 (6)	0.0256 (6)	−0.0005 (6)
C15	0.0407 (9)	0.0307 (8)	0.0294 (9)	−0.0036 (7)	0.0023 (7)	0.0016 (7)
C16	0.0266 (8)	0.0298 (8)	0.0319 (9)	0.0001 (6)	0.0027 (6)	0.0002 (7)
C21	0.0221 (7)	0.0305 (8)	0.0270 (8)	−0.0039 (6)	0.0020 (6)	−0.0027 (7)
C22	0.0351 (9)	0.0322 (9)	0.0364 (10)	−0.0002 (7)	0.0018 (7)	−0.0027 (7)
C23	0.0410 (10)	0.0352 (10)	0.0550 (13)	−0.0023 (8)	0.0095 (9)	−0.0120 (9)
C24	0.0364 (10)	0.0527 (12)	0.0479 (12)	−0.0120 (9)	0.0108 (9)	−0.0264 (10)
F24	0.0647 (9)	0.0721 (10)	0.0744 (10)	−0.0163 (8)	0.0103 (8)	−0.0485 (8)
C25	0.0344 (9)	0.0675 (14)	0.0292 (9)	−0.0095 (9)	0.0023 (8)	−0.0119 (9)
C26	0.0289 (8)	0.0439 (10)	0.0278 (9)	−0.0041 (7)	0.0029 (7)	−0.0008 (7)
C41	0.0227 (7)	0.0409 (9)	0.0327 (9)	−0.0019 (7)	0.0003 (6)	0.0000 (7)
C42	0.0262 (8)	0.0358 (9)	0.0359 (10)	−0.0046 (7)	0.0004 (7)	0.0046 (8)
C43	0.0276 (8)	0.0323 (8)	0.0341 (9)	0.0022 (7)	0.0022 (7)	0.0020 (7)
C31	0.0226 (7)	0.0364 (9)	0.0309 (9)	0.0012 (6)	0.0026 (6)	0.0005 (7)
C32	0.0300 (8)	0.0392 (9)	0.0334 (9)	0.0048 (7)	0.0013 (7)	0.0025 (8)
C33	0.0338 (9)	0.0545 (12)	0.0316 (9)	0.0006 (8)	−0.0019 (7)	−0.0019 (9)
C34	0.0359 (9)	0.0458 (11)	0.0458 (11)	−0.0066 (8)	0.0020 (8)	−0.0105 (9)
C35	0.0393 (10)	0.0342 (9)	0.0516 (12)	−0.0031 (8)	0.0031 (9)	0.0008 (9)
C36	0.0331 (9)	0.0392 (9)	0.0335 (9)	0.0003 (7)	−0.0012 (7)	0.0046 (8)
N51	0.0569 (11)	0.0434 (10)	0.0469 (11)	0.0060 (9)	−0.0031 (9)	0.0113 (8)
C52	0.0416 (10)	0.0388 (10)	0.0309 (9)	0.0023 (8)	0.0040 (7)	0.0052 (8)
C53	0.0299 (8)	0.0299 (8)	0.0271 (8)	−0.0083 (6)	−0.0002 (6)	−0.0008 (7)
C54	0.0387 (9)	0.0413 (10)	0.0342 (10)	−0.0121 (8)	0.0091 (8)	−0.0037 (8)
C55	0.0548 (12)	0.0545 (12)	0.0302 (10)	−0.0224 (10)	0.0054 (9)	0.0076 (9)
C56	0.0563 (13)	0.0447 (11)	0.0418 (12)	−0.0128 (10)	−0.0097 (10)	0.0161 (9)
C57	0.0280 (7)	0.0275 (8)	0.0279 (8)	−0.0049 (6)	−0.0006 (6)	−0.0020 (6)
O51	0.0428 (7)	0.0361 (6)	0.0298 (6)	0.0054 (6)	0.0086 (5)	0.0067 (5)
O52	0.0382 (7)	0.0389 (7)	0.0457 (8)	0.0061 (6)	0.0082 (6)	−0.0006 (6)

Geometric parameters (Å, º)

N1—C6	1.463 (2)	C24—F24	1.355 (2)
N1—C2	1.469 (2)	C24—C25	1.368 (3)
N1—C1	1.479 (2)	C25—C26	1.391 (3)
C2—C3	1.512 (2)	C25—H25	0.9500
C2—H2A	0.9900	C26—H26	0.9500
C2—H2B	0.9900	C41—C42	1.497 (3)
C3—N4	1.491 (2)	C41—H41A	0.9900
C3—H3A	0.9900	C41—H41B	0.9900
C3—H3B	0.9900	C42—C43	1.324 (3)
N4—C5	1.489 (2)	C42—H42	0.9500
N4—C41	1.501 (2)	C43—C31	1.467 (3)
N4—H4	0.9807	C43—H43	0.9500
C5—C6	1.516 (2)	C31—C32	1.393 (3)
C5—H5A	0.9900	C31—C36	1.402 (3)
C5—H5B	0.9900	C32—C33	1.384 (3)

C6—H6A	0.9900	C32—H32	0.9500
C6—H6B	0.9900	C33—C34	1.385 (3)
C1—C21	1.515 (2)	C33—H33	0.9500
C1—C11	1.524 (2)	C34—C35	1.386 (3)
C1—H1	1.0000	C34—H34	0.9500
C11—C16	1.388 (2)	C35—C36	1.384 (3)
C11—C12	1.396 (2)	C35—H35	0.9500
C12—C13	1.390 (3)	C36—H36	0.9500
C12—H12	0.9500	N51—C56	1.332 (3)
C13—C14	1.364 (3)	N51—C52	1.339 (3)
C13—H13	0.9500	C52—C53	1.386 (3)
C14—F14	1.370 (2)	C52—H52	0.9500
C14—C15	1.373 (3)	C53—C54	1.384 (2)
C15—C16	1.392 (3)	C53—C57	1.506 (2)
C15—H15	0.9500	C54—C55	1.383 (3)
C16—H16	0.9500	C54—H54	0.9500
C21—C26	1.394 (2)	C55—C56	1.371 (4)
C21—C22	1.397 (3)	C55—H55	0.9500
C22—C23	1.387 (3)	C56—H56	0.9500
C22—H22	0.9500	C57—O52	1.237 (2)
C23—C24	1.371 (4)	C57—O51	1.278 (2)
C23—H23	0.9500		

C6—N1—C2	108.19 (12)	C21—C22—H22	119.7
C6—N1—C1	113.38 (12)	C24—C23—C22	118.8 (2)
C2—N1—C1	109.77 (12)	C24—C23—H23	120.6
N1—C2—C3	111.08 (13)	C22—C23—H23	120.6
N1—C2—H2A	109.4	F24—C24—C25	119.0 (2)
C3—C2—H2A	109.4	F24—C24—C23	118.2 (2)
N1—C2—H2B	109.4	C25—C24—C23	122.72 (18)
C3—C2—H2B	109.4	C24—C25—C26	118.30 (19)
H2A—C2—H2B	108.0	C24—C25—H25	120.8
N4—C3—C2	110.27 (13)	C26—C25—H25	120.8
N4—C3—H3A	109.6	C25—C26—C21	121.03 (19)
C2—C3—H3A	109.6	C25—C26—H26	119.5
N4—C3—H3B	109.6	C21—C26—H26	119.5
C2—C3—H3B	109.6	C42—C41—N4	112.91 (15)
H3A—C3—H3B	108.1	C42—C41—H41A	109.0
C5—N4—C3	109.54 (12)	N4—C41—H41A	109.0
C5—N4—C41	109.36 (13)	C42—C41—H41B	109.0
C3—N4—C41	112.14 (13)	N4—C41—H41B	109.0
C5—N4—H4	108.3	H41A—C41—H41B	107.8
C3—N4—H4	107.8	C43—C42—C41	122.33 (17)
C41—N4—H4	109.6	C43—C42—H42	118.8
N4—C5—C6	110.88 (13)	C41—C42—H42	118.8
N4—C5—H5A	109.5	C42—C43—C31	128.20 (17)
C6—C5—H5A	109.5	C42—C43—H43	115.9
N4—C5—H5B	109.5	C31—C43—H43	115.9

C6—C5—H5B	109.5	C32—C31—C36	118.03 (17)
H5A—C5—H5B	108.1	C32—C31—C43	118.94 (16)
N1—C6—C5	109.75 (13)	C36—C31—C43	123.00 (16)
N1—C6—H6A	109.7	C33—C32—C31	121.50 (18)
C5—C6—H6A	109.7	C33—C32—H32	119.3
N1—C6—H6B	109.7	C31—C32—H32	119.3
C5—C6—H6B	109.7	C32—C33—C34	119.79 (19)
H6A—C6—H6B	108.2	C32—C33—H33	120.1
N1—C1—C21	112.03 (13)	C34—C33—H33	120.1
N1—C1—C11	110.05 (13)	C33—C34—C35	119.62 (19)
C21—C1—C11	110.90 (13)	C33—C34—H34	120.2
N1—C1—H1	107.9	C35—C34—H34	120.2
C21—C1—H1	107.9	C36—C35—C34	120.61 (19)
C11—C1—H1	107.9	C36—C35—H35	119.7
C16—C11—C12	118.57 (16)	C34—C35—H35	119.7
C16—C11—C1	121.68 (14)	C35—C36—C31	120.44 (18)
C12—C11—C1	119.65 (15)	C35—C36—H36	119.8
C13—C12—C11	121.12 (16)	C31—C36—H36	119.8
C13—C12—H12	119.4	C56—N51—C52	116.3 (2)
C11—C12—H12	119.4	N51—C52—C53	124.38 (19)
C14—C13—C12	117.95 (17)	N51—C52—H52	117.8
C14—C13—H13	121.0	C53—C52—H52	117.8
C12—C13—H13	121.0	C54—C53—C52	117.59 (17)
C13—C14—F14	118.32 (17)	C54—C53—C57	121.05 (17)
C13—C14—C15	123.42 (17)	C52—C53—C57	121.35 (16)
F14—C14—C15	118.25 (18)	C55—C54—C53	118.8 (2)
C14—C15—C16	117.93 (17)	C55—C54—H54	120.6
C14—C15—H15	121.0	C53—C54—H54	120.6
C16—C15—H15	121.0	C56—C55—C54	118.9 (2)
C11—C16—C15	120.99 (16)	C56—C55—H55	120.6
C11—C16—H16	119.5	C54—C55—H55	120.6
C15—C16—H16	119.5	N51—C56—C55	124.01 (19)
C26—C21—C22	118.54 (16)	N51—C56—H56	118.0
C26—C21—C1	119.76 (16)	C55—C56—H56	118.0
C22—C21—C1	121.69 (15)	O52—C57—O51	125.05 (17)
C23—C22—C21	120.62 (19)	O52—C57—C53	119.87 (16)
C23—C22—H22	119.7	O51—C57—C53	115.07 (15)

C6—N1—C2—C3	−61.39 (16)	C21—C22—C23—C24	0.3 (3)
C1—N1—C2—C3	174.41 (13)	C22—C23—C24—F24	−178.91 (18)
N1—C2—C3—N4	58.60 (17)	C22—C23—C24—C25	0.0 (3)
C2—C3—N4—C5	−54.81 (17)	F24—C24—C25—C26	178.74 (18)
C2—C3—N4—C41	−176.42 (14)	C23—C24—C25—C26	−0.1 (3)
C3—N4—C5—C6	55.99 (17)	C24—C25—C26—C21	0.1 (3)
C41—N4—C5—C6	179.26 (14)	C22—C21—C26—C25	0.1 (3)
C2—N1—C6—C5	61.43 (16)	C1—C21—C26—C25	−179.35 (16)
C1—N1—C6—C5	−176.56 (14)	C5—N4—C41—C42	−177.30 (14)
N4—C5—C6—N1	−60.11 (17)	C3—N4—C41—C42	−55.58 (19)

C6—N1—C1—C21	44.09 (18)	N4—C41—C42—C43	118.27 (19)
C6—N1—C1—C11	167.96 (13)	C41—C42—C43—C31	177.23 (16)
C2—N1—C1—C11	−70.92 (16)	C42—C43—C31—C32	−178.93 (18)
C2—N1—C1—C21	165.22 (13)	C42—C43—C31—C36	−0.6 (3)
N1—C1—C11—C16	−33.4 (2)	C36—C31—C32—C33	−0.8 (3)
C21—C1—C11—C16	91.08 (18)	C43—C31—C32—C33	177.64 (17)
N1—C1—C11—C12	150.17 (15)	C31—C32—C33—C34	0.4 (3)
C21—C1—C11—C12	−85.31 (18)	C32—C33—C34—C35	0.4 (3)
C16—C11—C12—C13	−0.3 (2)	C33—C34—C35—C36	−0.8 (3)
C1—C11—C12—C13	176.25 (15)	C34—C35—C36—C31	0.4 (3)
C11—C12—C13—C14	1.3 (3)	C32—C31—C36—C35	0.4 (3)
C12—C13—C14—F14	177.30 (15)	C43—C31—C36—C35	−177.98 (18)
C12—C13—C14—C15	−1.7 (3)	C56—N51—C52—C53	1.3 (3)
C13—C14—C15—C16	1.0 (3)	N51—C52—C53—C54	−0.3 (3)
F14—C14—C15—C16	−177.96 (16)	N51—C52—C53—C57	178.99 (18)
C12—C11—C16—C15	−0.4 (3)	C52—C53—C54—C55	−1.3 (3)
C1—C11—C16—C15	−176.87 (15)	C57—C53—C54—C55	179.41 (17)
C14—C15—C16—C11	0.1 (3)	C53—C54—C55—C56	1.9 (3)
N1—C1—C21—C26	−111.11 (17)	C52—N51—C56—C55	−0.6 (3)
C11—C1—C21—C26	125.50 (17)	C54—C55—C56—N51	−0.9 (3)
N1—C1—C21—C22	69.4 (2)	C54—C53—C57—O52	2.9 (2)
C11—C1—C21—C22	−54.0 (2)	C52—C53—C57—O52	−176.37 (17)
C26—C21—C22—C23	−0.3 (3)	C54—C53—C57—O51	−176.63 (16)
C1—C21—C22—C23	179.18 (16)	C52—C53—C57—O51	4.1 (2)

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 represent the centroids of the C11–C16 and C31–C36 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O51	0.98	1.58	2.5630 (19)	175
C3—H3*B*···O52^{i}	0.99	2.53	3.440 (2)	153
C13—H13···O52^{ii}	0.95	2.57	3.442 (2)	152
C56—H56···O51^{iii}	0.95	2.34	3.236 (3)	158
C26—H26···*Cg*1^{iv}	0.95	2.81	3.758 (2)	173
C55—H55···*Cg*2^{v}	0.95	2.85	3.567 (2)	133

Symmetry codes: (i) *x*, −*y*+1, *z*+1/2; (ii) *x*−1, −*y*+1, *z*+1/2; (iii) *x*, −*y*+2, *z*−1/2; (iv) *x*, −*y*+1, *z*−1/2; (v) *x*, *y*, *z*−1.

(II) 1-[Bis(4-fluorophenyl)methyl]-4-[(2*E*)-3-phenylprop-2-en-1-yl]piperazine-1,4-diium bis(4-methylbenzenesulfonate) dihydrate

Crystal data

$C_{26}H_{28}F_2N_2^{2+}·2C_7H_7O_3S^{-}·2H_2O$
M_r = 784.91
Monoclinic, $P2_1/c$
a = 10.0546 (5) Å
b = 14.8338 (6) Å
c = 26.9437 (12) Å
β = 106.497 (3)°
V = 3853.2 (3) Å^3
Z = 4
$F(000)$ = 1656
D_x = 1.353 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9580 reflections
θ = 1.6–28.4°

μ = 0.20 mm^{-1}
T = 200 K

Block, yellow
0.59 × 0.43 × 0.24 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.877, T_{max} = 0.953
45646 measured reflections

7212 independent reflections
6219 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 25.6°, θ_{min} = 2.1°
h = −12→12
k = −15→18
l = −32→32

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.202
S = 1.09
7212 reflections
527 parameters
27 restraints

Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 8.0533P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.9062 (3)	0.31590 (17)	0.06845 (9)	0.0283 (5)	
H1	0.9988	0.3286	0.0707	0.034*	
C2	0.8798 (4)	0.3563 (2)	0.11553 (12)	0.0377 (8)	
H2A	0.9473	0.3313	0.1467	0.045*	
H2B	0.7857	0.3391	0.1167	0.045*	
C3	0.8915 (3)	0.4569 (2)	0.11658 (12)	0.0329 (7)	
H3A	0.8675	0.4802	0.1474	0.040*	
H3B	0.9888	0.4740	0.1198	0.040*	
N4	0.7998 (3)	0.49940 (19)	0.06970 (10)	0.0374 (6)	
H4	0.7026	0.4838	0.0691	0.045*	
C5	0.8239 (4)	0.4592 (2)	0.02266 (12)	0.0376 (8)	
H5A	0.9185	0.4751	0.0213	0.045*	
H5B	0.7570	0.4853	−0.0083	0.045*	
C6	0.8088 (4)	0.3587 (2)	0.02114 (13)	0.0421 (8)	
H6A	0.8289	0.3351	−0.0103	0.050*	
H6B	0.7120	0.3426	0.0193	0.050*	
C1	0.8877 (4)	0.2133 (2)	0.06603 (13)	0.0376 (8)	
H1A	0.7879	0.2008	0.0629	0.045*	
C11	0.9731 (4)	0.1704 (2)	0.11671 (14)	0.0411 (8)	
C12	0.9029 (4)	0.1445 (3)	0.15121 (15)	0.0464 (9)	

H12	0.8061	0.1555	0.1435	0.056*
C13	0.9716 (5)	0.1025 (3)	0.19714 (16)	0.0549 (10)
H13	0.9228	0.0848	0.2210	0.066*
C14	1.1094 (5)	0.0870 (3)	0.20764 (16)	0.0572 (11)
F14	1.1764 (3)	0.04445 (19)	0.25255 (11)	0.0858 (10)
C15	1.1850 (5)	0.1137 (3)	0.17454 (19)	0.0610 (12)
H15	1.2822	0.1039	0.1830	0.073*
C16	1.1131 (4)	0.1556 (3)	0.12814 (16)	0.0491 (9)
H16	1.1618	0.1740	0.1044	0.059*
C21	0.9177 (4)	0.1744 (2)	0.01823 (13)	0.0377 (8)
C22	1.0266 (4)	0.1995 (3)	−0.00073 (16)	0.0511 (10)
H22	1.0890	0.2450	0.0167	0.061*
C23	1.0464 (5)	0.1601 (3)	−0.04430 (16)	0.0542 (10)
H23	1.1211	0.1780	−0.0571	0.065*
C24	0.9575 (5)	0.0957 (3)	−0.06822 (14)	0.0503 (10)
F24	0.9777 (4)	0.05713 (19)	−0.11165 (10)	0.0848 (10)
C25	0.8505 (5)	0.0685 (3)	−0.05213 (16)	0.0588 (11)
H25	0.7905	0.0222	−0.0701	0.071*
C26	0.8279 (4)	0.1087 (3)	−0.00872 (16)	0.0504 (9)
H26	0.7504	0.0910	0.0026	0.061*
C41	0.8089 (4)	0.5998 (2)	0.06908 (14)	0.0440 (8)
H41A	0.9029	0.6170	0.0677	0.053*
H41B	0.7418	0.6225	0.0371	0.053*
C42	0.7812 (4)	0.6449 (2)	0.11408 (14)	0.0432 (8)
H42	0.6939	0.6343	0.1201	0.052*
C43	0.8675 (4)	0.6978 (3)	0.14586 (15)	0.0457 (9)
H43	0.9579	0.7021	0.1416	0.055*
C31	0.8407 (4)	0.7523 (3)	0.18798 (14)	0.0442 (8)
C32	0.9371 (5)	0.8177 (3)	0.21029 (16)	0.0580 (11)
H32	1.0175	0.8247	0.1988	0.070*
C33	0.9191 (6)	0.8722 (3)	0.24818 (18)	0.0676 (13)
H33	0.9861	0.9174	0.2622	0.081*
C34	0.8081 (6)	0.8634 (3)	0.26634 (17)	0.0710 (15)
H34	0.7970	0.9018	0.2931	0.085*
C35	0.7098 (5)	0.7972 (4)	0.24544 (19)	0.0681 (13)
H35	0.6314	0.7895	0.2581	0.082*
C36	0.7275 (4)	0.7427 (3)	0.20607 (16)	0.0527 (10)
H36	0.6600	0.6981	0.1914	0.063*
C51	1.3052 (3)	0.6677 (2)	0.17881 (13)	0.0366 (7)
C52	1.2814 (4)	0.7583 (3)	0.16840 (15)	0.0446 (8)
H52	1.2474	0.7782	0.1336	0.054*
C53	1.3065 (4)	0.8197 (3)	0.20801 (16)	0.0507 (9)
H53	1.2896	0.8818	0.2003	0.061*
C54	1.3564 (4)	0.7923 (3)	0.25945 (16)	0.0504 (9)
C55	1.3787 (5)	0.7012 (3)	0.26940 (15)	0.0523 (10)
H55	1.4118	0.6810	0.3042	0.063*
C56	1.3537 (4)	0.6388 (3)	0.22950 (14)	0.0484 (9)
H56	1.3698	0.5765	0.2370	0.058*

C57	1.3887 (6)	0.8599 (4)	0.30303 (19)	0.0741 (14)	
H57A	1.3970	0.8287	0.3358	0.111*	
H57B	1.3139	0.9045	0.2970	0.111*	
H57C	1.4763	0.8904	0.3046	0.111*	
S51	1.27821 (10)	0.59086 (6)	0.12647 (3)	0.0400 (2)	
O51	1.2760 (4)	0.50202 (19)	0.14856 (11)	0.0621 (8)	
O52	1.3909 (3)	0.60300 (19)	0.10373 (12)	0.0601 (8)	
O53	1.1460 (3)	0.6137 (2)	0.09039 (10)	0.0662 (9)	
C61	0.4319 (4)	0.1735 (3)	−0.00551 (18)	0.0413 (11)	0.832 (6)
C62	0.3808 (17)	0.0869 (7)	−0.0143 (4)	0.093 (2)	0.832 (6)
H62	0.3444	0.0576	0.0104	0.112*	0.832 (6)
C63	0.3830 (13)	0.0428 (6)	−0.0596 (4)	0.092 (4)	0.832 (6)
H63	0.3522	−0.0180	−0.0645	0.110*	0.832 (6)
C64	0.4279 (13)	0.0839 (6)	−0.0970 (3)	0.0534 (13)	0.832 (6)
C65	0.4758 (6)	0.1721 (4)	−0.0882 (2)	0.0484 (15)	0.832 (6)
H65	0.5067	0.2027	−0.1138	0.058*	0.832 (6)
C66	0.4789 (5)	0.2158 (3)	−0.04249 (19)	0.0450 (13)	0.832 (6)
H66	0.5139	0.2755	−0.0367	0.054*	0.832 (6)
C67	0.4262 (16)	0.0347 (6)	−0.1462 (4)	0.070 (2)	0.832 (6)
H67A	0.4667	0.0732	−0.1676	0.105*	0.832 (6)
H67B	0.3303	0.0199	−0.1652	0.105*	0.832 (6)
H67C	0.4804	−0.0209	−0.1376	0.105*	0.832 (6)
S61	0.44568 (17)	0.22444 (13)	0.05538 (6)	0.0442 (4)	0.832 (6)
O61	0.3748 (4)	0.3104 (2)	0.04318 (14)	0.0566 (11)	0.832 (6)
O62	0.3801 (4)	0.1655 (3)	0.08433 (15)	0.0681 (12)	0.832 (6)
O63	0.5873 (5)	0.2398 (5)	0.0767 (2)	0.097 (2)	0.832 (6)
C61A	0.474 (2)	0.1737 (10)	−0.0054 (6)	0.0413 (11)	0.168 (6)
C62A	0.397 (8)	0.095 (3)	−0.0121 (15)	0.093 (2)	0.168 (6)
H62A	0.3742	0.0678	0.0164	0.112*	0.168 (6)
C63A	0.353 (7)	0.056 (4)	−0.0611 (16)	0.092 (4)	0.168 (6)
H63A	0.2792	0.0139	−0.0684	0.110*	0.168 (6)
C64A	0.413 (7)	0.078 (3)	−0.0988 (13)	0.0534 (13)	0.168 (6)
C65A	0.502 (4)	0.152 (2)	−0.0898 (8)	0.0484 (15)	0.168 (6)
H65A	0.5517	0.1670	−0.1138	0.058*	0.168 (6)
C66A	0.518 (3)	0.2049 (15)	−0.0460 (7)	0.0450 (13)	0.168 (6)
H66A	0.5591	0.2628	−0.0441	0.054*	0.168 (6)
C67A	0.405 (9)	0.015 (4)	−0.1434 (19)	0.070 (2)	0.168 (6)
H67D	0.3240	0.0304	−0.1723	0.105*	0.168 (6)
H67E	0.3960	−0.0471	−0.1324	0.105*	0.168 (6)
H67F	0.4894	0.0206	−0.1544	0.105*	0.168 (6)
S61A	0.4738 (9)	0.2443 (6)	0.0478 (3)	0.0442 (4)	0.168 (6)
O61A	0.4807 (16)	0.3360 (7)	0.0291 (6)	0.059 (5)*	0.168 (6)
O62A	0.3450 (13)	0.2298 (11)	0.0612 (6)	0.067 (6)*	0.168 (6)
O63A	0.5974 (10)	0.2273 (9)	0.0855 (5)	0.017 (3)*	0.168 (6)
O71	1.1663 (3)	0.37595 (19)	0.07577 (12)	0.0563 (7)	
H71A	1.1873	0.4171	0.0985	0.084*	
H71B	1.2430	0.3652	0.0700	0.090*	
O81	0.5371 (3)	0.4699 (2)	0.07130 (16)	0.0782 (11)	

H81B	0.4924	0.5051	0.0850	0.117*
H81A	0.4824	0.4292	0.0563	0.117*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0293 (13)	0.0278 (13)	0.0288 (13)	−0.0005 (10)	0.0099 (10)	−0.0034 (10)
C2	0.050 (2)	0.0381 (18)	0.0283 (16)	0.0069 (15)	0.0164 (15)	−0.0004 (13)
C3	0.0369 (17)	0.0332 (17)	0.0273 (15)	0.0053 (13)	0.0070 (13)	−0.0024 (13)
N4	0.0484 (17)	0.0359 (15)	0.0300 (14)	0.0117 (13)	0.0144 (12)	0.0002 (12)
C5	0.0432 (19)	0.0415 (19)	0.0284 (16)	0.0103 (15)	0.0108 (14)	−0.0007 (14)
C6	0.049 (2)	0.044 (2)	0.0312 (17)	0.0087 (16)	0.0092 (15)	−0.0010 (15)
C1	0.0378 (18)	0.0334 (18)	0.0418 (19)	−0.0049 (14)	0.0114 (15)	−0.0050 (14)
C11	0.053 (2)	0.0281 (17)	0.0437 (19)	0.0048 (15)	0.0162 (17)	−0.0046 (14)
C12	0.056 (2)	0.039 (2)	0.047 (2)	0.0028 (17)	0.0188 (18)	0.0022 (16)
C13	0.076 (3)	0.042 (2)	0.049 (2)	0.002 (2)	0.022 (2)	0.0085 (18)
C14	0.082 (3)	0.033 (2)	0.045 (2)	0.003 (2)	0.001 (2)	0.0006 (17)
F14	0.110 (2)	0.0607 (17)	0.0622 (16)	0.0123 (16)	−0.0149 (16)	0.0141 (13)
C15	0.046 (2)	0.045 (2)	0.083 (3)	0.0035 (18)	0.004 (2)	−0.012 (2)
C16	0.056 (2)	0.037 (2)	0.056 (2)	−0.0032 (17)	0.0189 (19)	−0.0028 (17)
C21	0.049 (2)	0.0317 (17)	0.0335 (17)	0.0078 (15)	0.0142 (15)	−0.0001 (14)
C22	0.056 (2)	0.047 (2)	0.055 (2)	−0.0161 (18)	0.0226 (19)	−0.0180 (18)
C23	0.074 (3)	0.049 (2)	0.052 (2)	−0.002 (2)	0.037 (2)	−0.0044 (18)
C24	0.079 (3)	0.037 (2)	0.0364 (19)	0.0094 (19)	0.0184 (19)	−0.0044 (15)
F24	0.150 (3)	0.0631 (17)	0.0510 (15)	−0.0019 (18)	0.0443 (17)	−0.0222 (13)
C25	0.075 (3)	0.044 (2)	0.052 (2)	−0.015 (2)	0.009 (2)	−0.0171 (19)
C26	0.053 (2)	0.040 (2)	0.061 (2)	−0.0046 (17)	0.022 (2)	0.0034 (18)
C41	0.056 (2)	0.0346 (18)	0.0409 (19)	0.0125 (16)	0.0140 (17)	0.0048 (15)
C42	0.051 (2)	0.0348 (19)	0.045 (2)	0.0131 (16)	0.0159 (17)	0.0001 (15)
C43	0.044 (2)	0.045 (2)	0.051 (2)	0.0082 (17)	0.0189 (17)	0.0088 (17)
C31	0.053 (2)	0.042 (2)	0.0365 (18)	0.0099 (17)	0.0110 (16)	0.0059 (15)
C32	0.063 (3)	0.062 (3)	0.050 (2)	−0.002 (2)	0.016 (2)	0.010 (2)
C33	0.090 (4)	0.050 (3)	0.051 (2)	−0.011 (2)	0.001 (2)	0.000 (2)
C34	0.112 (4)	0.056 (3)	0.040 (2)	0.031 (3)	0.013 (3)	−0.006 (2)
C35	0.064 (3)	0.083 (3)	0.065 (3)	0.027 (3)	0.032 (2)	0.016 (3)
C36	0.053 (2)	0.048 (2)	0.054 (2)	0.0001 (18)	0.0090 (19)	0.0028 (18)
C51	0.0362 (17)	0.0393 (18)	0.0359 (17)	0.0018 (14)	0.0130 (14)	0.0037 (14)
C52	0.052 (2)	0.041 (2)	0.0402 (19)	0.0053 (16)	0.0121 (16)	0.0039 (16)
C53	0.056 (2)	0.040 (2)	0.059 (2)	0.0058 (17)	0.022 (2)	0.0019 (18)
C54	0.054 (2)	0.054 (2)	0.049 (2)	−0.0008 (18)	0.0243 (18)	−0.0107 (18)
C55	0.065 (3)	0.059 (2)	0.0348 (19)	−0.005 (2)	0.0172 (18)	0.0042 (17)
C56	0.064 (2)	0.044 (2)	0.0393 (19)	−0.0007 (18)	0.0185 (18)	0.0058 (16)
C57	0.095 (4)	0.071 (3)	0.061 (3)	−0.003 (3)	0.030 (3)	−0.019 (2)
S51	0.0485 (5)	0.0403 (5)	0.0339 (4)	−0.0020 (4)	0.0159 (4)	0.0013 (3)
O51	0.100 (2)	0.0417 (15)	0.0421 (15)	−0.0197 (15)	0.0159 (15)	−0.0003 (12)
O52	0.0704 (19)	0.0503 (17)	0.076 (2)	−0.0065 (14)	0.0471 (17)	−0.0141 (14)
O53	0.0642 (19)	0.093 (2)	0.0365 (14)	0.0181 (17)	0.0066 (13)	−0.0071 (15)
C61	0.021 (3)	0.045 (2)	0.060 (2)	0.0073 (18)	0.0144 (19)	−0.0026 (18)

C62	0.153 (7)	0.058 (4)	0.100 (4)	−0.043 (4)	0.088 (5)	−0.025 (3)
C63	0.160 (9)	0.046 (4)	0.094 (4)	−0.028 (6)	0.076 (5)	−0.019 (3)
C64	0.057 (4)	0.050 (3)	0.053 (2)	0.013 (2)	0.014 (2)	0.0022 (19)
C65	0.040 (3)	0.057 (4)	0.044 (2)	0.006 (3)	0.0053 (19)	0.011 (2)
C66	0.030 (3)	0.044 (2)	0.054 (2)	0.001 (2)	−0.001 (2)	0.0033 (19)
C67	0.093 (7)	0.062 (6)	0.054 (3)	0.010 (4)	0.018 (3)	0.000 (4)
S61	0.0298 (7)	0.0456 (8)	0.0606 (7)	−0.0028 (6)	0.0183 (5)	−0.0034 (6)
O61	0.058 (2)	0.053 (2)	0.060 (2)	0.0118 (16)	0.0186 (17)	−0.0062 (16)
O62	0.072 (3)	0.073 (3)	0.068 (2)	0.000 (2)	0.034 (2)	0.008 (2)
O63	0.068 (3)	0.138 (6)	0.091 (4)	0.017 (3)	0.034 (3)	−0.017 (4)
C61A	0.021 (3)	0.045 (2)	0.060 (2)	0.0073 (18)	0.0144 (19)	−0.0026 (18)
C62A	0.153 (7)	0.058 (4)	0.100 (4)	−0.043 (4)	0.088 (5)	−0.025 (3)
C63A	0.160 (9)	0.046 (4)	0.094 (4)	−0.028 (6)	0.076 (5)	−0.019 (3)
C64A	0.057 (4)	0.050 (3)	0.053 (2)	0.013 (2)	0.014 (2)	0.0022 (19)
C65A	0.040 (3)	0.057 (4)	0.044 (2)	0.006 (3)	0.0053 (19)	0.011 (2)
C66A	0.030 (3)	0.044 (2)	0.054 (2)	0.001 (2)	−0.001 (2)	0.0033 (19)
C67A	0.093 (7)	0.062 (6)	0.054 (3)	0.010 (4)	0.018 (3)	0.000 (4)
S61A	0.0298 (7)	0.0456 (8)	0.0606 (7)	−0.0028 (6)	0.0183 (5)	−0.0034 (6)
O71	0.0462 (15)	0.0511 (16)	0.0750 (19)	−0.0082 (12)	0.0228 (14)	−0.0225 (14)
O81	0.0590 (19)	0.065 (2)	0.128 (3)	0.0021 (16)	0.056 (2)	−0.015 (2)

Geometric parameters (Å, º)

N1—C2	1.493 (4)	C36—H36	0.9500
N1—C6	1.509 (4)	C51—C52	1.380 (5)
N1—C1	1.532 (4)	C51—C56	1.382 (5)
N1—H1	0.9355	C51—S51	1.773 (4)
C2—C3	1.497 (5)	C52—C53	1.371 (5)
C2—H2A	0.9900	C52—H52	0.9500
C2—H2B	0.9900	C53—C54	1.394 (6)
C3—N4	1.477 (4)	C53—H53	0.9500
C3—H3A	0.9900	C54—C55	1.384 (6)
C3—H3B	0.9900	C54—C57	1.507 (6)
N4—C5	1.482 (4)	C55—C56	1.387 (6)
N4—C41	1.493 (4)	C55—H55	0.9500
N4—H4	0.9998	C56—H56	0.9500
C5—C6	1.497 (5)	C57—H57A	0.9800
C5—H5A	0.9900	C57—H57B	0.9800
C5—H5B	0.9900	C57—H57C	0.9800
C6—H6A	0.9900	S51—O52	1.444 (3)
C6—H6B	0.9900	S51—O53	1.446 (3)
C1—C21	1.518 (5)	S51—O51	1.449 (3)
C1—C11	1.531 (5)	C61—C66	1.370 (6)
C1—H1A	1.0000	C61—C62	1.379 (7)
C11—C16	1.370 (5)	C61—S61	1.776 (4)
C11—C12	1.372 (5)	C62—C63	1.390 (8)
C12—C13	1.382 (6)	C62—H62	0.9500
C12—H12	0.9500	C63—C64	1.361 (7)

C13—C14	1.352 (7)	C63—H63	0.9500
C13—H13	0.9500	C64—C65	1.390 (7)
C14—F14	1.361 (5)	C64—C67	1.508 (6)
C14—C15	1.384 (7)	C65—C66	1.384 (7)
C15—C16	1.400 (6)	C65—H65	0.9500
C15—H15	0.9500	C66—H66	0.9500
C16—H16	0.9500	C67—H67A	0.9800
C21—C22	1.384 (5)	C67—H67B	0.9800
C21—C26	1.386 (5)	C67—H67C	0.9800
C22—C23	1.376 (5)	S61—O63	1.395 (5)
C22—H22	0.9500	S61—O62	1.448 (4)
C23—C24	1.341 (6)	S61—O61	1.452 (4)
C23—H23	0.9500	C61A—C66A	1.373 (7)
C24—C25	1.332 (6)	C61A—C62A	1.383 (8)
C24—F24	1.368 (4)	C61A—S61A	1.773 (6)
C25—C26	1.388 (6)	C62A—C63A	1.392 (10)
C25—H25	0.9500	C62A—H62A	0.9500
C26—H26	0.9500	C63A—C64A	1.362 (8)
C41—C42	1.479 (5)	C63A—H63A	0.9500
C41—H41A	0.9900	C64A—C65A	1.392 (9)
C41—H41B	0.9900	C64A—C67A	1.509 (8)
C42—C43	1.297 (6)	C65A—C66A	1.384 (8)
C42—H42	0.9500	C65A—H65A	0.9500
C43—C31	1.479 (5)	C66A—H66A	0.9500
C43—H43	0.9500	C67A—H67D	0.9800
C31—C36	1.367 (6)	C67A—H67E	0.9800
C31—C32	1.382 (6)	C67A—H67F	0.9800
C32—C33	1.353 (7)	S61A—O63A	1.388 (6)
C32—H32	0.9500	S61A—O62A	1.456 (6)
C33—C34	1.346 (8)	S61A—O61A	1.458 (6)
C33—H33	0.9500	O71—H71A	0.8475
C34—C35	1.394 (8)	O71—H71B	0.8448
C34—H34	0.9500	O81—H81B	0.8387
C35—C36	1.384 (6)	O81—H81A	0.8393
C35—H35	0.9500		

C2—N1—C6	108.6 (2)	C33—C34—H34	120.4
C2—N1—C1	112.7 (2)	C35—C34—H34	120.4
C6—N1—C1	109.9 (2)	C36—C35—C34	119.3 (4)
C2—N1—H1	106.2	C36—C35—H35	120.3
C6—N1—H1	111.4	C34—C35—H35	120.3
C1—N1—H1	108.0	C31—C36—C35	120.9 (4)
N1—C2—C3	112.6 (3)	C31—C36—H36	119.5
N1—C2—H2A	109.1	C35—C36—H36	119.5
C3—C2—H2A	109.1	C52—C51—C56	119.7 (3)
N1—C2—H2B	109.1	C52—C51—S51	119.1 (3)
C3—C2—H2B	109.1	C56—C51—S51	121.2 (3)
H2A—C2—H2B	107.8	C53—C52—C51	120.4 (3)

N4—C3—C2	112.5 (3)	C53—C52—H52	119.8
N4—C3—H3A	109.1	C51—C52—H52	119.8
C2—C3—H3A	109.1	C52—C53—C54	121.1 (4)
N4—C3—H3B	109.1	C52—C53—H53	119.5
C2—C3—H3B	109.1	C54—C53—H53	119.5
H3A—C3—H3B	107.8	C55—C54—C53	118.0 (4)
C3—N4—C5	110.2 (2)	C55—C54—C57	120.7 (4)
C3—N4—C41	114.2 (3)	C53—C54—C57	121.2 (4)
C5—N4—C41	111.5 (3)	C54—C55—C56	121.2 (4)
C3—N4—H4	106.5	C54—C55—H55	119.4
C5—N4—H4	106.9	C56—C55—H55	119.4
C41—N4—H4	107.0	C51—C56—C55	119.6 (4)
N4—C5—C6	112.6 (3)	C51—C56—H56	120.2
N4—C5—H5A	109.1	C55—C56—H56	120.2
C6—C5—H5A	109.1	C54—C57—H57A	109.5
N4—C5—H5B	109.1	C54—C57—H57B	109.5
C6—C5—H5B	109.1	H57A—C57—H57B	109.5
H5A—C5—H5B	107.8	C54—C57—H57C	109.5
C5—C6—N1	111.1 (3)	H57A—C57—H57C	109.5
C5—C6—H6A	109.4	H57B—C57—H57C	109.5
N1—C6—H6A	109.4	O52—S51—O53	111.57 (19)
C5—C6—H6B	109.4	O52—S51—O51	113.15 (19)
N1—C6—H6B	109.4	O53—S51—O51	111.8 (2)
H6A—C6—H6B	108.0	O52—S51—C51	107.21 (17)
C21—C1—C11	113.7 (3)	O53—S51—C51	106.72 (17)
C21—C1—N1	111.3 (3)	O51—S51—C51	105.94 (16)
C11—C1—N1	110.2 (3)	C66—C61—C62	119.4 (4)
C21—C1—H1A	107.1	C66—C61—S61	121.7 (3)
C11—C1—H1A	107.1	C62—C61—S61	118.8 (4)
N1—C1—H1A	107.1	C61—C62—C63	119.4 (5)
C16—C11—C12	119.8 (4)	C61—C62—H62	120.3
C16—C11—C1	123.2 (3)	C63—C62—H62	120.3
C12—C11—C1	117.0 (3)	C64—C63—C62	122.0 (5)
C11—C12—C13	120.7 (4)	C64—C63—H63	119.0
C11—C12—H12	119.7	C62—C63—H63	119.0
C13—C12—H12	119.7	C63—C64—C65	117.9 (4)
C14—C13—C12	119.1 (4)	C63—C64—C67	120.7 (5)
C14—C13—H13	120.5	C65—C64—C67	121.5 (5)
C12—C13—H13	120.5	C66—C65—C64	120.8 (4)
C13—C14—F14	118.9 (4)	C66—C65—H65	119.6
C13—C14—C15	122.3 (4)	C64—C65—H65	119.6
F14—C14—C15	118.8 (4)	C61—C66—C65	120.5 (4)
C14—C15—C16	117.6 (4)	C61—C66—H66	119.7
C14—C15—H15	121.2	C65—C66—H66	119.7
C16—C15—H15	121.2	C64—C67—H67A	109.5
C11—C16—C15	120.6 (4)	C64—C67—H67B	109.5
C11—C16—H16	119.7	H67A—C67—H67B	109.5
C15—C16—H16	119.7	C64—C67—H67C	109.5

C22—C21—C26	117.5 (3)	H67A—C67—H67C	109.5
C22—C21—C1	125.4 (3)	H67B—C67—H67C	109.5
C26—C21—C1	117.1 (3)	O63—S61—O62	116.4 (4)
C23—C22—C21	121.5 (4)	O63—S61—O61	109.1 (4)
C23—C22—H22	119.3	O62—S61—O61	112.5 (2)
C21—C22—H22	119.3	O63—S61—C61	104.6 (3)
C24—C23—C22	118.3 (4)	O62—S61—C61	108.2 (2)
C24—C23—H23	120.8	O61—S61—C61	105.1 (2)
C22—C23—H23	120.8	C66A—C61A—C62A	118.3 (7)
C25—C24—C23	123.3 (4)	C66A—C61A—S61A	121.2 (7)
C25—C24—F24	118.8 (4)	C62A—C61A—S61A	118.5 (8)
C23—C24—F24	117.9 (4)	C61A—C62A—C63A	119.1 (9)
C24—C25—C26	119.0 (4)	C61A—C62A—H62A	120.5
C24—C25—H25	120.5	C63A—C62A—H62A	120.5
C26—C25—H25	120.5	C64A—C63A—C62A	121.5 (11)
C21—C26—C25	120.3 (4)	C64A—C63A—H63A	119.3
C21—C26—H26	119.8	C62A—C63A—H63A	119.3
C25—C26—H26	119.8	C63A—C64A—C65A	117.1 (7)
C42—C41—N4	114.5 (3)	C63A—C64A—C67A	120.7 (9)
C42—C41—H41A	108.6	C65A—C64A—C67A	121.2 (11)
N4—C41—H41A	108.6	C66A—C65A—C64A	120.4 (8)
C42—C41—H41B	108.6	C66A—C65A—H65A	119.8
N4—C41—H41B	108.6	C64A—C65A—H65A	119.8
H41A—C41—H41B	107.6	C61A—C66A—C65A	120.4 (7)
C43—C42—C41	124.6 (4)	C61A—C66A—H66A	119.8
C43—C42—H42	117.7	C65A—C66A—H66A	119.8
C41—C42—H42	117.7	C64A—C67A—H67D	109.5
C42—C43—C31	127.2 (4)	C64A—C67A—H67E	109.5
C42—C43—H43	116.4	H67D—C67A—H67E	109.5
C31—C43—H43	116.4	C64A—C67A—H67F	109.5
C36—C31—C32	118.0 (4)	H67D—C67A—H67F	109.5
C36—C31—C43	124.6 (4)	H67E—C67A—H67F	109.5
C32—C31—C43	117.4 (4)	O63A—S61A—O62A	117.7 (7)
C33—C32—C31	121.3 (4)	O63A—S61A—O61A	107.6 (6)
C33—C32—H32	119.3	O62A—S61A—O61A	110.9 (6)
C31—C32—H32	119.3	O63A—S61A—C61A	106.3 (6)
C34—C33—C32	121.2 (5)	O62A—S61A—C61A	108.4 (6)
C34—C33—H33	119.4	O61A—S61A—C61A	105.2 (6)
C32—C33—H33	119.4	H71A—O71—H71B	102.4
C33—C34—C35	119.2 (4)	H81B—O81—H81A	107.5

C6—N1—C2—C3	−55.3 (4)	C33—C34—C35—C36	−0.8 (7)
C1—N1—C2—C3	−177.3 (3)	C32—C31—C36—C35	0.2 (6)
N1—C2—C3—N4	55.4 (4)	C43—C31—C36—C35	−179.4 (4)
C2—C3—N4—C5	−53.2 (4)	C34—C35—C36—C31	0.8 (7)
C2—C3—N4—C41	−179.7 (3)	C56—C51—C52—C53	0.4 (6)
C3—N4—C5—C6	54.7 (4)	S51—C51—C52—C53	−177.5 (3)
C41—N4—C5—C6	−177.3 (3)	C51—C52—C53—C54	0.0 (6)

N4—C5—C6—N1	−57.2 (4)	C52—C53—C54—C55	−0.6 (6)
C2—N1—C6—C5	55.9 (4)	C52—C53—C54—C57	177.9 (4)
C1—N1—C6—C5	179.6 (3)	C53—C54—C55—C56	0.6 (6)
C6—N1—C1—C21	59.7 (3)	C57—C54—C55—C56	−177.8 (4)
C2—N1—C1—C11	−51.9 (4)	C52—C51—C56—C55	−0.4 (6)
C2—N1—C1—C21	−179.0 (3)	S51—C51—C56—C55	177.5 (3)
C6—N1—C1—C11	−173.2 (3)	C54—C55—C56—C51	−0.2 (6)
C21—C1—C11—C16	46.3 (5)	C52—C51—S51—O52	73.3 (3)
N1—C1—C11—C16	−79.4 (4)	C56—C51—S51—O52	−104.6 (3)
C21—C1—C11—C12	−132.4 (3)	C52—C51—S51—O53	−46.4 (3)
N1—C1—C11—C12	101.8 (4)	C56—C51—S51—O53	135.8 (3)
C16—C11—C12—C13	−0.9 (6)	C52—C51—S51—O51	−165.6 (3)
C1—C11—C12—C13	177.9 (3)	C56—C51—S51—O51	16.5 (4)
C11—C12—C13—C14	−0.2 (6)	C66—C61—C62—C63	2.5 (17)
C12—C13—C14—F14	−179.0 (4)	S61—C61—C62—C63	−173.3 (9)
C12—C13—C14—C15	1.6 (6)	C61—C62—C63—C64	−3.3 (18)
C13—C14—C15—C16	−2.0 (6)	C62—C63—C64—C65	1.7 (15)
F14—C14—C15—C16	178.7 (4)	C62—C63—C64—C67	−178.7 (13)
C12—C11—C16—C15	0.5 (6)	C63—C64—C65—C66	0.7 (13)
C1—C11—C16—C15	−178.2 (3)	C67—C64—C65—C66	−178.9 (9)
C14—C15—C16—C11	0.8 (6)	C62—C61—C66—C65	−0.2 (11)
C11—C1—C21—C22	−82.7 (4)	S61—C61—C66—C65	175.5 (4)
N1—C1—C21—C22	42.4 (5)	C64—C65—C66—C61	−1.4 (9)
C11—C1—C21—C26	97.7 (4)	C66—C61—S61—O63	−58.5 (5)
N1—C1—C21—C26	−137.2 (3)	C62—C61—S61—O63	117.3 (10)
C26—C21—C22—C23	−0.8 (6)	C66—C61—S61—O62	176.8 (4)
C1—C21—C22—C23	179.6 (4)	C62—C61—S61—O62	−7.5 (10)
C21—C22—C23—C24	−0.4 (7)	C66—C61—S61—O61	56.4 (4)
C22—C23—C24—C25	0.5 (7)	C62—C61—S61—O61	−127.8 (9)
C22—C23—C24—F24	179.7 (4)	C66A—C61A—C62A—C63A	−8 (7)
C23—C24—C25—C26	0.5 (7)	S61A—C61A—C62A—C63A	157 (4)
F24—C24—C25—C26	−178.7 (4)	C61A—C62A—C63A—C64A	18 (7)
C22—C21—C26—C25	1.9 (6)	C62A—C63A—C64A—C65A	−12 (6)
C1—C21—C26—C25	−178.5 (4)	C62A—C63A—C64A—C67A	157 (7)
C24—C25—C26—C21	−1.7 (7)	C63A—C64A—C65A—C66A	−5 (7)
C3—N4—C41—C42	−56.2 (4)	C67A—C64A—C65A—C66A	−174 (5)
C5—N4—C41—C42	178.0 (3)	C62A—C61A—C66A—C65A	−9 (5)
N4—C41—C42—C43	121.6 (4)	S61A—C61A—C66A—C65A	−173 (3)
C41—C42—C43—C31	172.9 (3)	C64A—C65A—C66A—C61A	16 (6)
C42—C43—C31—C36	12.6 (6)	C66A—C61A—S61A—O63A	−95 (2)
C42—C43—C31—C32	−167.1 (4)	C62A—C61A—S61A—O63A	101 (4)
C36—C31—C32—C33	−1.3 (6)	C66A—C61A—S61A—O62A	137 (2)
C43—C31—C32—C33	178.3 (4)	C62A—C61A—S61A—O62A	−27 (4)
C31—C32—C33—C34	1.4 (7)	C66A—C61A—S61A—O61A	19 (2)
C32—C33—C34—C35	−0.3 (7)	C62A—C61A—S61A—O61A	−145 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O71	0.93	1.79	2.716 (4)	169
N4—H4···O81	1.00	1.69	2.690 (4)	173
O71—H71*A*···O51	0.85	1.88	2.708 (4)	167
O71—H71*B*···O61^{i}	0.84	1.87	2.675 (5)	160
O81—H81*A*···O61	0.84	2.05	2.852 (5)	161
O81—H81*B*···O52^{ii}	0.84	1.92	2.748 (4)	167
C1—H1*A*···O63	1.00	2.23	3.139 (7)	151
C2—H2*B*···O63	0.99	2.47	3.314 (7)	143
C6—H6*A*···O53^{iii}	0.99	2.37	3.191 (5)	140
C16—H16···O62^{i}	0.95	2.41	3.228 (6)	144
C22—H22···O71	0.95	2.49	3.381 (5)	156
C34—H34···O51^{iv}	0.95	2.42	3.362 (6)	169
C41—H41*A*···O53	0.99	2.35	3.280 (5)	157
C41—H41*B*···O61^{v}	0.99	2.37	3.341 (5)	167

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*−1, *y*, *z*; (iii) −*x*+2, −*y*+1, −*z*; (iv) −*x*+2, *y*+1/2, −*z*+1/2; (v) −*x*+1, −*y*+1, −*z*.